EnGen Institute

Institute Director

William Hollier

SAVING THE GREAT BARRIER REEF:

Hydrogen production that sequesters C02 and reduces ocean acidification

All-Energy Australia '09

8 Oct 2009

EnGen Institute - Activities

www.engen.org.au

EnGen Institute is a not-for-profit perpetual trust for research and education which is a registered charity with deductible gift recipient status.

EnGen Institute develops advanced life support technology for communities and has research programs in generative engineering (knowledge based engineering and design automation), energy generation and environment generation.

The energy generation program develops ocean energy and hydrogen energy technology.

The Institute's approach is based on -
– Goal-oriented applied research
– Technology development and transfer
– Research collaboration, co-ordination and management

This research is a collaboration with –
Dr Greg Rau, Marine Science, USC & Lawrence Livermore National Laboratories
Dr Andrew Dicks, Dept of Chemistry, University of Queensland (fuel cell authority)

- Hydrogen Technology

Hydrogen Economy Drivers

Long term environmental drivers to the Hydrogen Economy

- climate change - the need to reduce carbon emissions
- peak oil – the increase in cost of oil for transport
  - and the need to keep oil for chemical processes (eg pharmaceuticals, textiles, food)
- pollution – increasing 'smog' or airborne hydrocarbon and particulate levels in major cities

Technical drivers related to renewable energy

- need for long distance transmission of energy (hydrogen pipelines)
  - more energy efficient than the transmission of electricity via power lines
- electricity can only be stored in small volumes (batteries)
  - H_2 pipelines can store TWh
- power lines are not divisible (a circuit) and not relocatable
  - but H_2 bulk shipping is both

Hydrogen Economy Barriers

H_2 is a very small, fast, simple and reactive molecule

and consequently has –

- Low energy density by volume
- High energy density by weight
  - which results in storage and transport inefficiency

Tube Trailer delivery and storage modules

The high cost of electrolysers is why producing H2 from renewable energy is expensive and why hydrogen is produce largely by reforming methane releasing CO2

Practical transport of hydrogen includes the use of receiver modules for safe and efficient storage of gaseous hydrogen at the user's site.

Praxair, Inc.

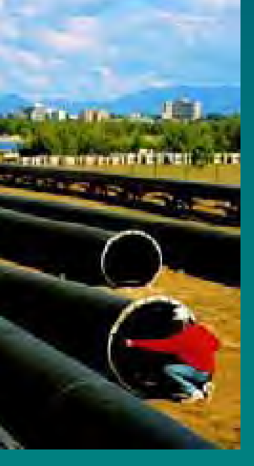
A new process to cost-effectively convert renewable energy (electricity) to hydrogen would be a major step towards the Hydrogen Economy – a process that was carbon negative would be even better – then bulk, low cost RE would be needed .

Hydrogen pipelines

H_2 is a very small, fast, simple and reactive molecule

and consequently has –

- potential leakage & storage problems
  (solved with new plastic pipes and liners)
- low viscosity (low pipeline pumping losses)



" In transporting hydrogen gas in plastic pipe the technical report mentioned in 1 above indicates that PVC and PE pipes manufactured in accordance with ASTM D2513-81 have good chemical resistance. Those pipes would appear to be appropriate for hydrogen."

Richard L. Beam
Associate Director for Pipeline Safety Regulation
Materials Transportation Bureau

Hydrogen pipelines

AIR LIQUIDE

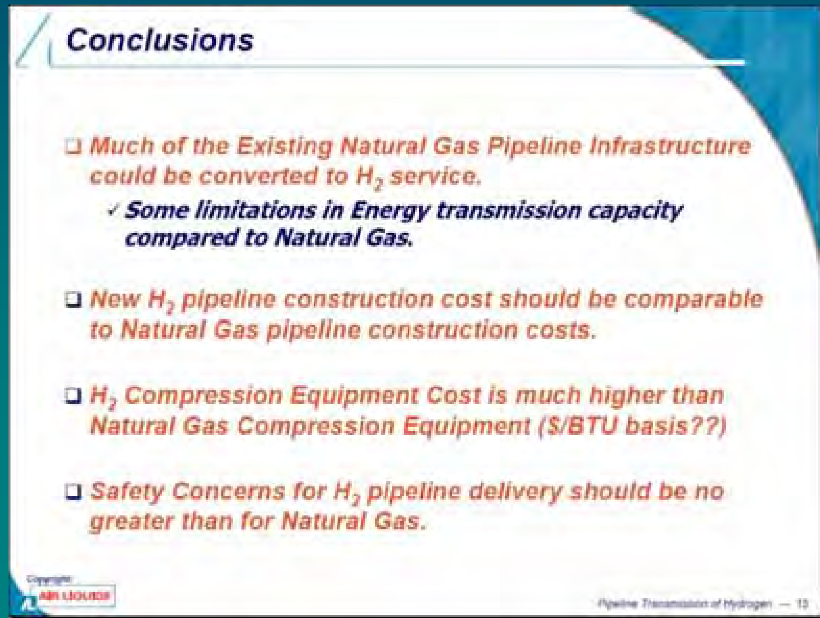
Hydrogen Delivery Technologies and Systems

Pipeline Transmission of Hydrogen

Strategic Initiatives for Hydrogen Delivery Workshop ■ May 7-8, 2003

U.S. Department of Energy ■ Hydrogen, Fuel Cells, and Infrastructure Technologies Program

Existing gas pipes retro-fitted with plastic liners



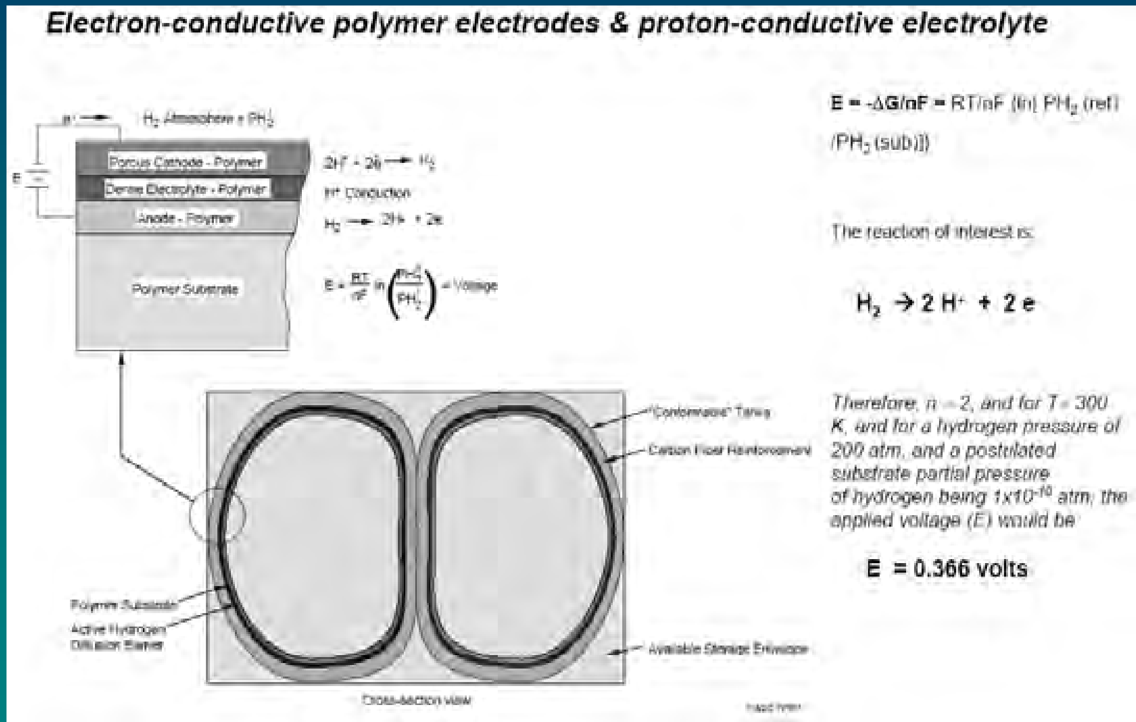
Conclusions

- Much of the Existing Natural Gas Pipeline Infrastructure could be converted to H_2 service.
  - ✓ Some limitations in Energy transmission capacity compared to Natural Gas.
- New H_2 pipeline construction cost should be comparable to Natural Gas pipeline construction costs.
- H_2 Compression Equipment Cost is much higher than Natural Gas Compression Equipment ($/BTU basis??)
- Safety Concerns for H_2 pipeline delivery should be no greater than for Natural Gas.

Pipeline Transmission of Hydrogen — 13

Over long distances - hydrogen pipelines deliver energy more cost effectively than powerlines

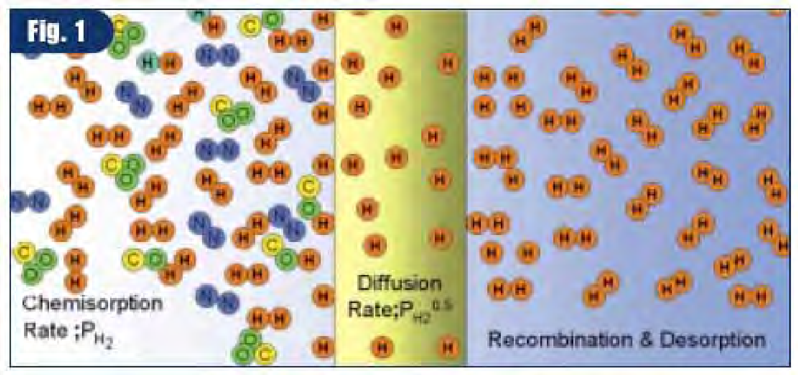
Shipping Hydrogen



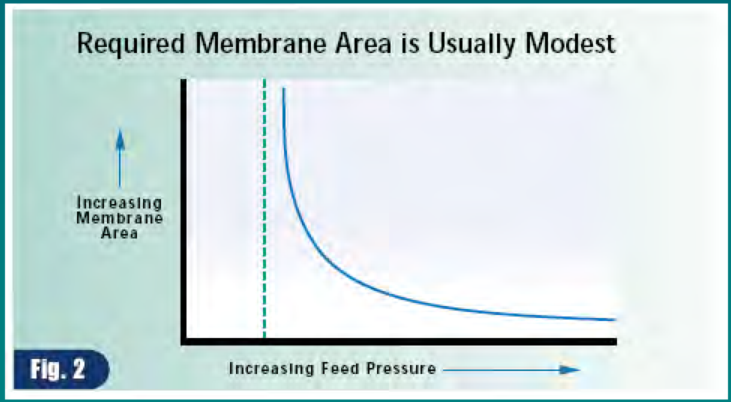
Active hydrogen diffusion barrier

Recovering Hydrogen from Gas Mixtures

Gas Separation



Concurrent pipeline transport or tanker shipping of gas mixtures with hydrogen extraction at customer site



Hydrogen for cleaner combustion

H_2 is a very small, fast, simple and reactive molecule
and consequently has –
- faster flame speed (speeds up combustion of other fuels)
- 'negative emissions' (can clean ambient air of smog)

• environmental benefit is greatest when hydrogen is mixed with LPG or CNG, petrol or diesel, or bio-fuels

• 6 % hydrogen gives
- more power,
- better economy and
- cleaner combustion
(Uni. Of Austin Texas) →

TEST RESULTS

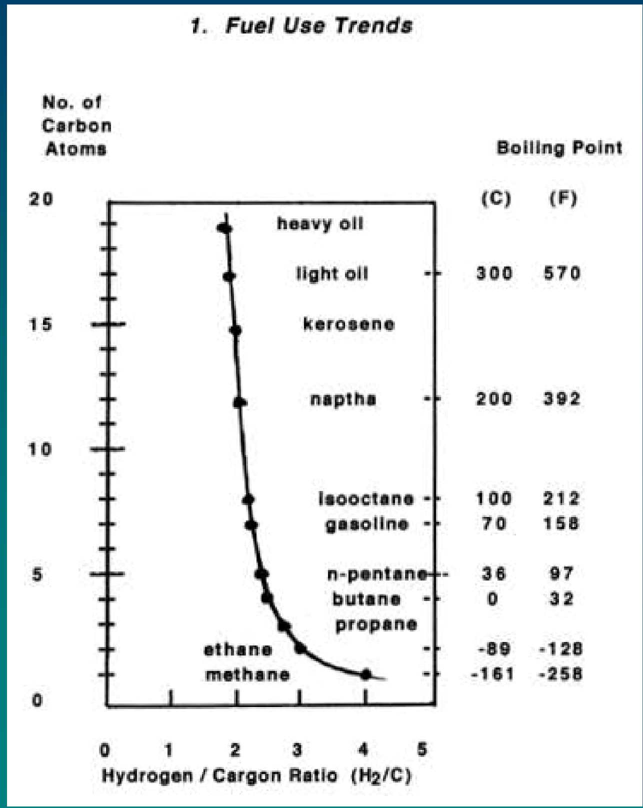
AMBIENT AIR TEST:			
	28 ppm HC (hydrocarbons)	**0.00 ppm CO** (Carbon Monoxide)	**1.0 ppm NO** (Nitrogen Monoxide)
FORKLIFT ENGINE WITH UNTHROTTLED AIR AND HYDROGEN OPERATION:			
Idle:	**16 ppm HC**	**0.00 ppm CO**	**1.0 ppm NO**
Full Power:	**3 ppm HC**	**0.00 ppm CO**	**2.0 ppm NO**
USING GASOLINE AS FUEL IN THE SAME ENGINE:			
Idle:	**219 ppm HC**	**27,000 ppm CO**	**410 ppm NO**
Full Power:	**206 ppm HC**	**7,300 ppm CO**	**105 ppm NO**

Hydrogen for cleaner combustion

Long term driver towards the Hydrogen Economy is the

⇒ trend to hydrogen rich, low carbon fuels

mixtures of methane (LNG/CNG) and hydrogen will have H_2/C ratios extending well beyond 4 towards pure hydrogen



- Marine Energy

MARINE ENERGY RESOURCE

- Oceans cover
  - 71% of the planet

- Marine Energy
  - 2 types
    - GRAVITY driven
    - SOLAR INFLUX driven

Marine Technologies

- **GRAVITY driven**
  - Tidal Range
  - Tidal Current

- **SOLAR INFLUX driven**
  - OTEC
  - Wave
  - Ocean Current
  - Osmotic Power
  - Offshore Wind

- **Ocean Sequestration**
  - Abyssal plane sequestration
  - Subsea Geo-sequestration
  - AWL (Augmented Weathering of Limestone)

- Seawater electrolysis

The technologies shown in aqua will be described. They can be combined in a mission to –
'Save the Great Barrier Reef'

Tidal Current Energy

- Solar, Wind & Wave v Tidal Current

	Solar PV	Wind	Wave	Tidal Current
Development Status	Early Commercial	Commercial	Pre-Commercial	Pre-Commercial
Source	Sun	Uneven solar heating	Wind blowing over water	Gravity of moon & sun
Annual Average Power Density	200-300 watts/m²	400-600 watts/m²	20-25+ kW/m (West Coast) 5-15 kW/m (East Coast)	5-10 kW/m² (Northern Australia) 1-2 kW/m² (SA, Vic)
Intermittency	Day-night; clouds, haze, and humidity	Atmospheric fronts and storms (local winds only)	Sea (local winds) and swell (from distant storms)	Diurnal and semi-diurnal (advancing ~50 min./day)
Predictability	Minutes	Hours	Days	Centuries

Solar - kW
Wind & Wave - MW
Tidal Current - GW

Sea Water is 837 times more dense than air.

Tidal Current power energy density is orders of magnitude greater than wind power –

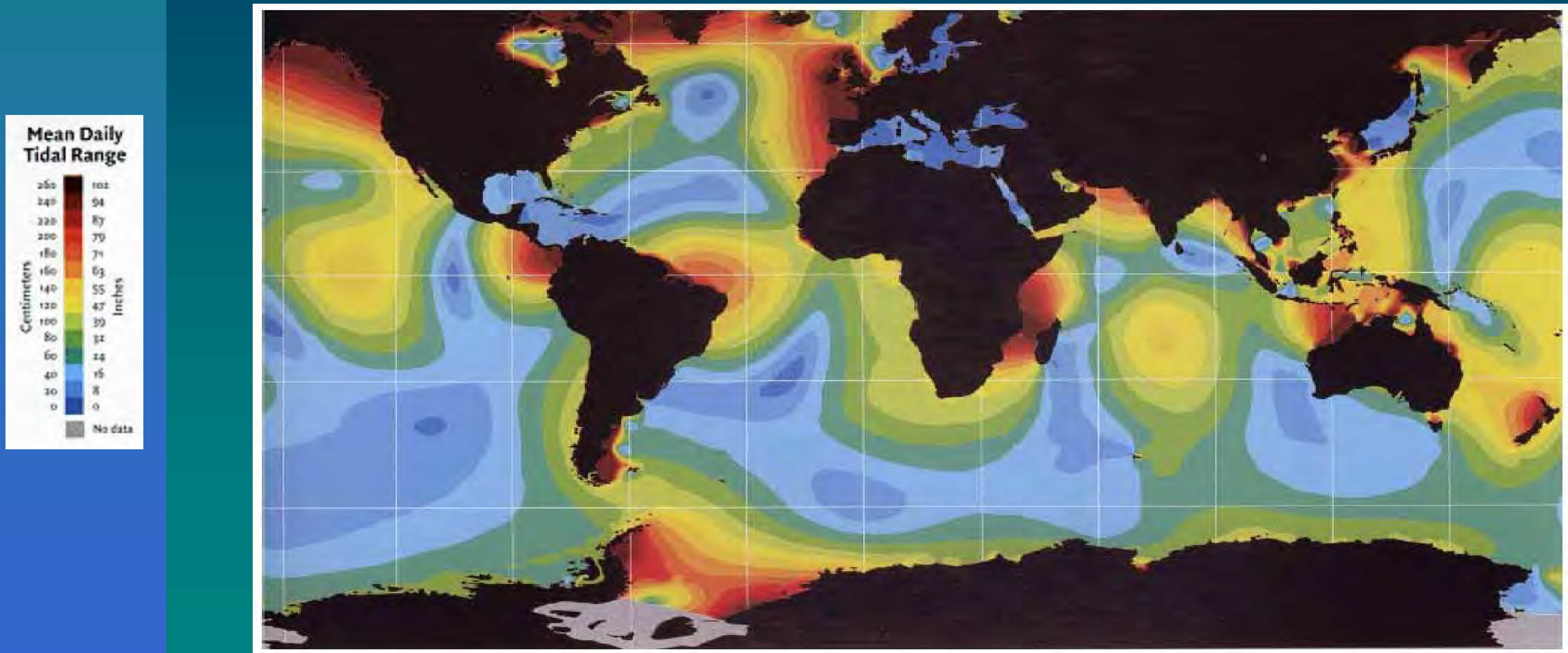
Wind turbine ≈ 10 kg/s/m²
Tidal turbine ≈ 3 ton/s/m²

Comparing 'Apples with Apples' -

in 10 meter deep sea - Tidal Current Energy = **100 kW per lineal meter**
in 100 meter deep sea - Tidal Current Energy = **1 MW per lineal meter**
in 100 meter deep sea - 8 knots, 25% efficiency = **1 GW per kilometre**

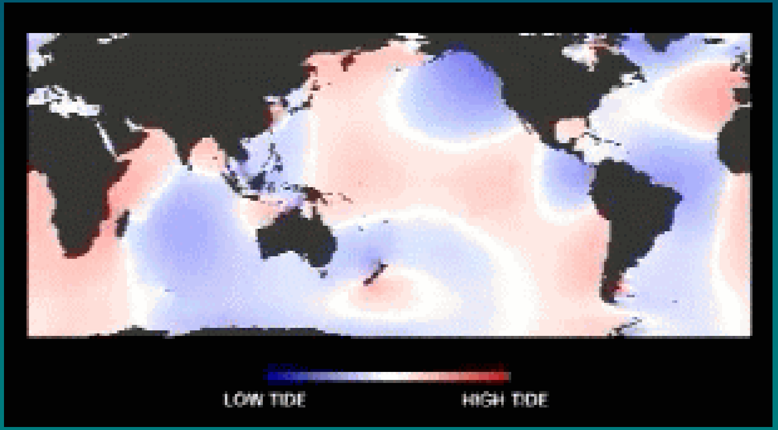
Tidal Resource

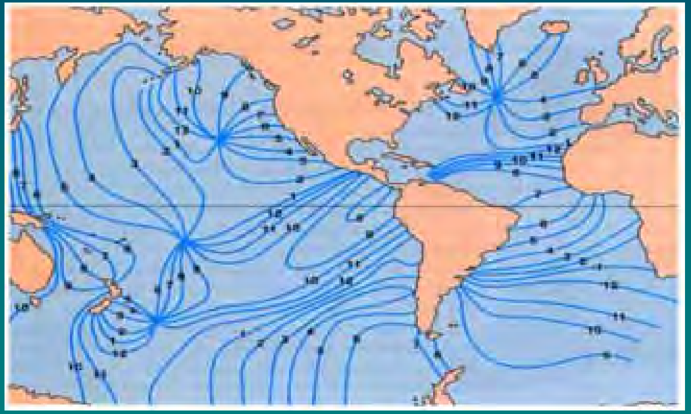
- The majority of the resource is in remote locations



GRAVITY driven Marine Energy

- Tidal Currents
  - Dynamic model





- Climate Effects

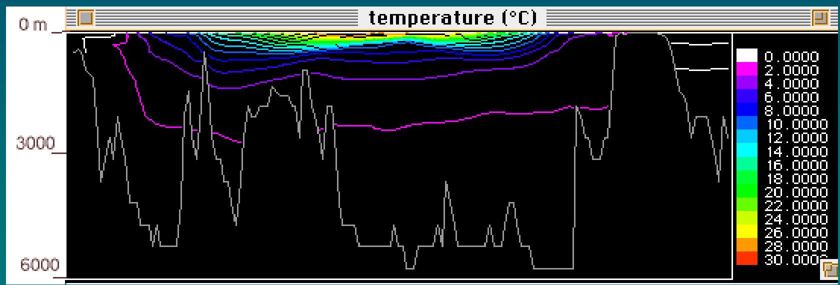
  - SOLAR INFLUX Driven

Marine Energy Technology Benefits

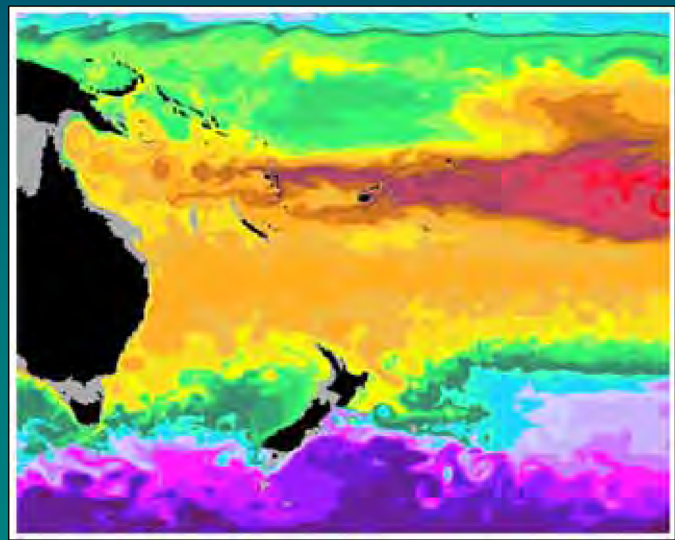
- Can counteract major Marine Climate Change effects
  - Reducing atmospheric GHG emissions will be too slow
- Hot Acidic Oceans – Short Term Impact
  - Coral Reef Bleaching
  - Declining in shell fish
- Rapid Climate Change – Medium Term Impact
  - Hot equatorial currents melt ice caps, dilute seas, effect ocean conveyor
  - Decline in deep ocean circulation is already happening
  - Meridional Overturning – now 1 of the 4 USA marine research priority investigations
- Ocean Anoxic Events – Long Term Impact
  - Onset due to major vulcanism OR
  - High greenhouse temperatures (wind & rain pattern shift, forests burn, methane hydrates, etc)
  - Local anoxic zones already exist
  - Hydrogen Sulphide – asphyxiation
  - Loss of Ozone layer – genetic damage

Hot Acidic Oceans

- Climate Change – Coral reefs as lead indicators
- Great Barrier Reef generates $6B/annum – tourism, fisheries etc



Note: the hot ocean currents are at the surface with cooler water below



Hot Acidic Oceans

- Climate Change – Coral reefs as lead indicators

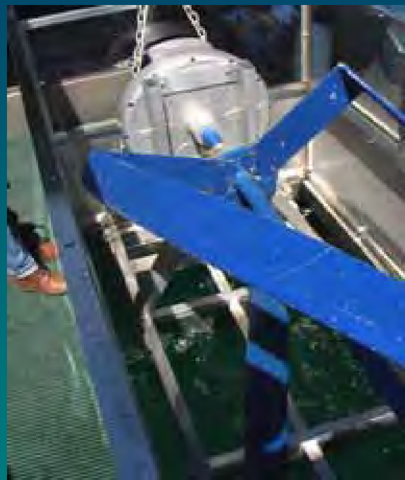
Tidal and hot ocean currents enter the reef through passages and both can be slowed with tidal turbines that can also pump up cooler water

- Our Research

Tidal Stream – Cross-flow Turbines

Helical Turbine – complementary development work in Australia

submersible generator &
power electronics



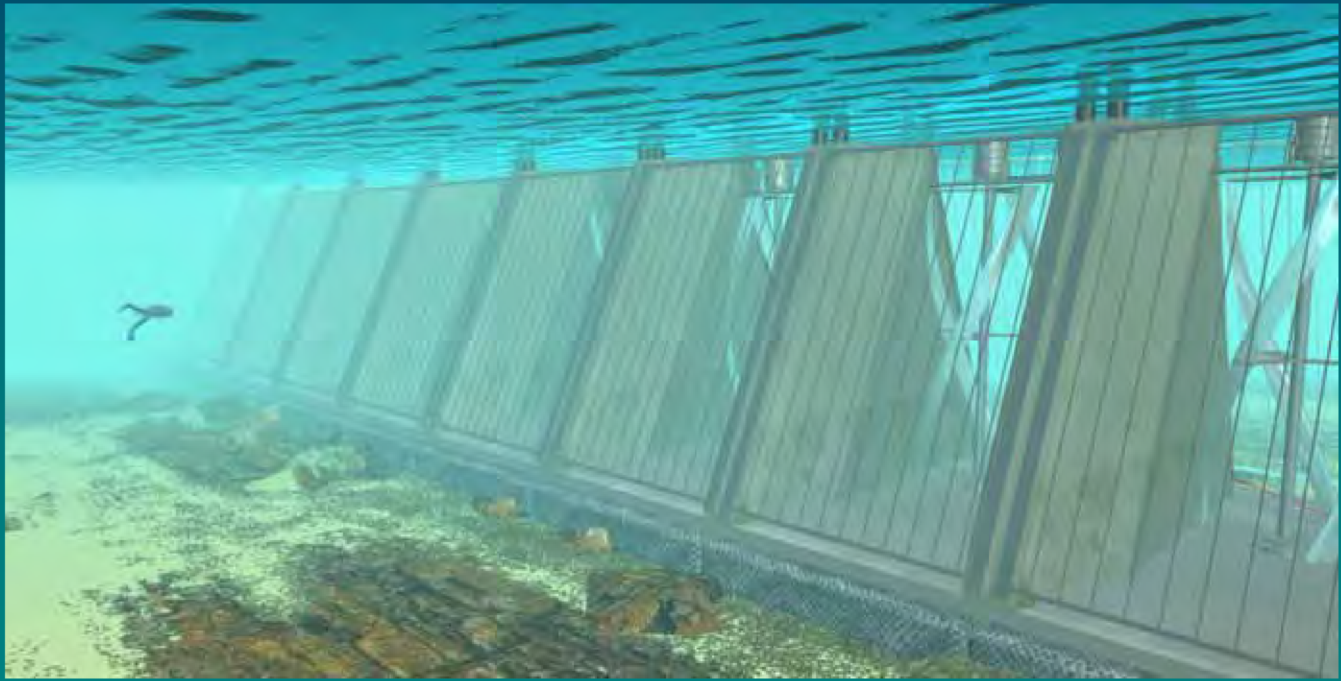
EnGen Institute -

- spin-off development company in 2006

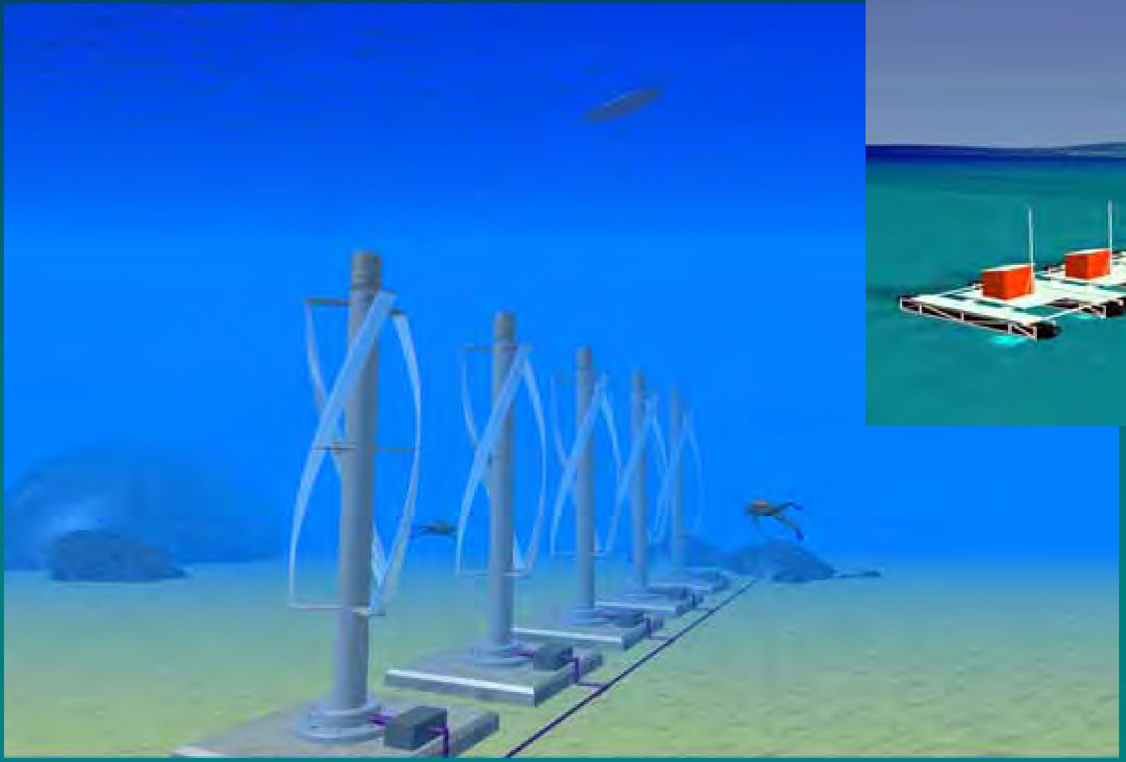
'HydroGen Power Industries Pty Ltd'

HydroGen Power Industries – Tidal Jetty

- Suitable for inshore locations



HydroGen Power Industries



Hot Acidic Oceans

- Tidal Turbines can be applied to cool the sea surface waters

- But what about increasing ocean acidity?
  - that can be addressed with AWL technology
  - 'Accelerated Weathering of Limestone' greatly increases the speed of the natural process that would eventually absorb CO2 and lower ocean acidity

- The following slides provided by Dr Greg Rau explain the rationale, mechanism and expected outcomes from AWL

- AWL Technology

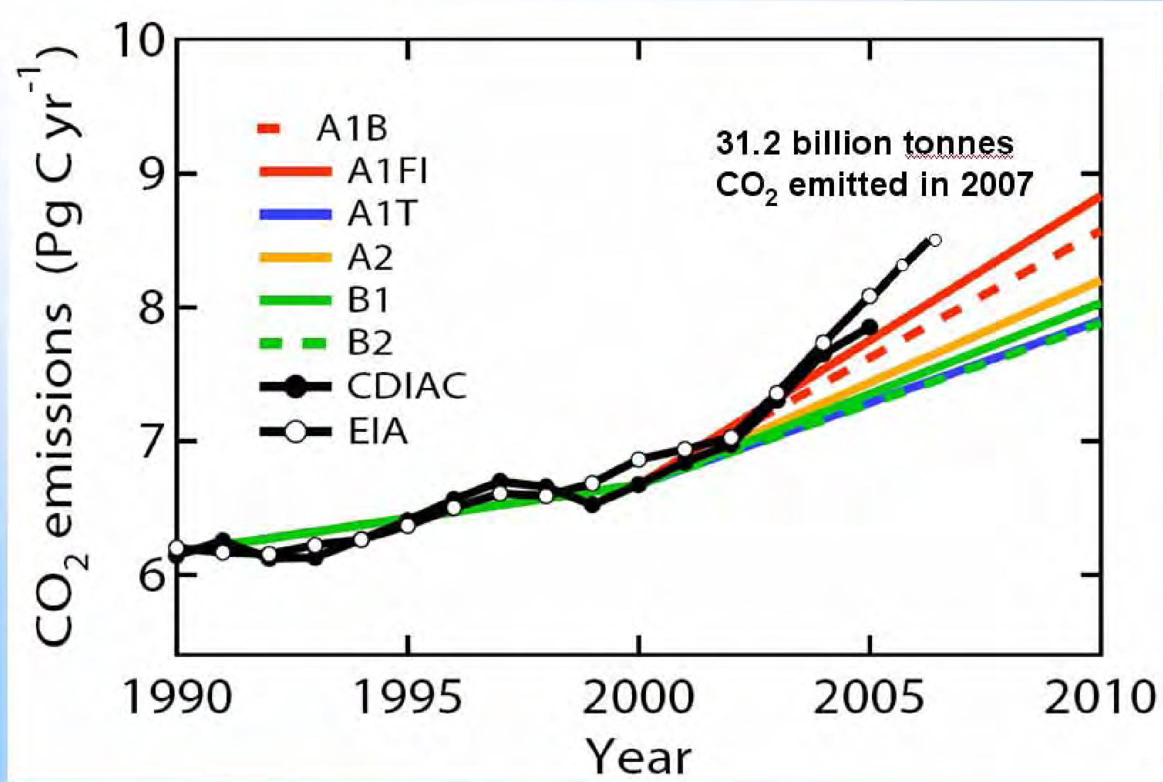
Electrochemical CO_2 Mitigation with Carbon-Negative H_2 Production

Greg H. Rau
Institute of Marine Sciences, University of California, Santa Cruz, and
Carbon Management Program, Lawrence Livermore National Laboratory
rau4@llnl.gov

The Electrochemical Society Meeting
San Francisco, May 26, 2009

Efforts to reverse CO_2 emissions have thus far failed:

Emissions now well above worst case scenarios



Accelerated Weathering of Limestone

Wet limestone scrubbing of flue gas:

$$CO_2 + H_2O + CaCO_3 \text{ ---> } Ca^{2+} + 2HCO_3^-$$

Advantages:

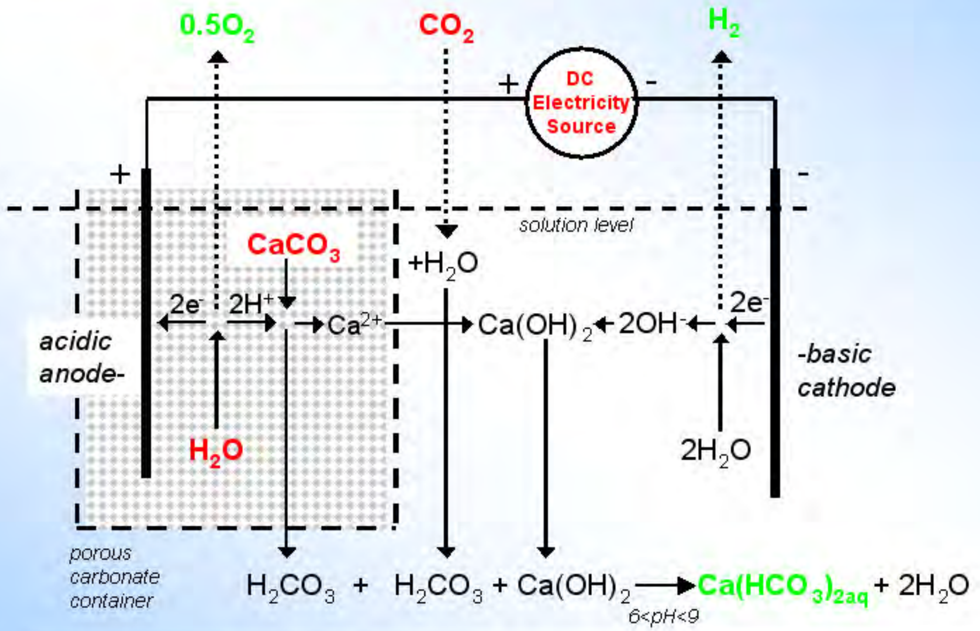
- Abundant reactants, benign products
- Low cost, low-tech, and low energy; applicable to developing countries
- Analogous to current SO_2 mitigation

Limitations:

- Requires elevated sources of CO_2, only rlevant to point sources
- Reaction is reversible if end solution exposed to air
- Not applicable everywhere; local H_2O and $CaCO_3$ supply/transport issues

Are there other ways to more widely employ abundant mineral carbonates for chemistry-based CO_2 mitigation?

Formation of $Ca(OH)_2$ Coupled With Saline Electrolysis, H_2 Production, and CO_2 Absorption



$CaCO_3$ as well as H_2O split

Net reaction: $CaCO_3 + H_2O + CO_2 + DC$ ---> $0.5O_2 + H_2 + Ca(HCO_3)_{2aq}$

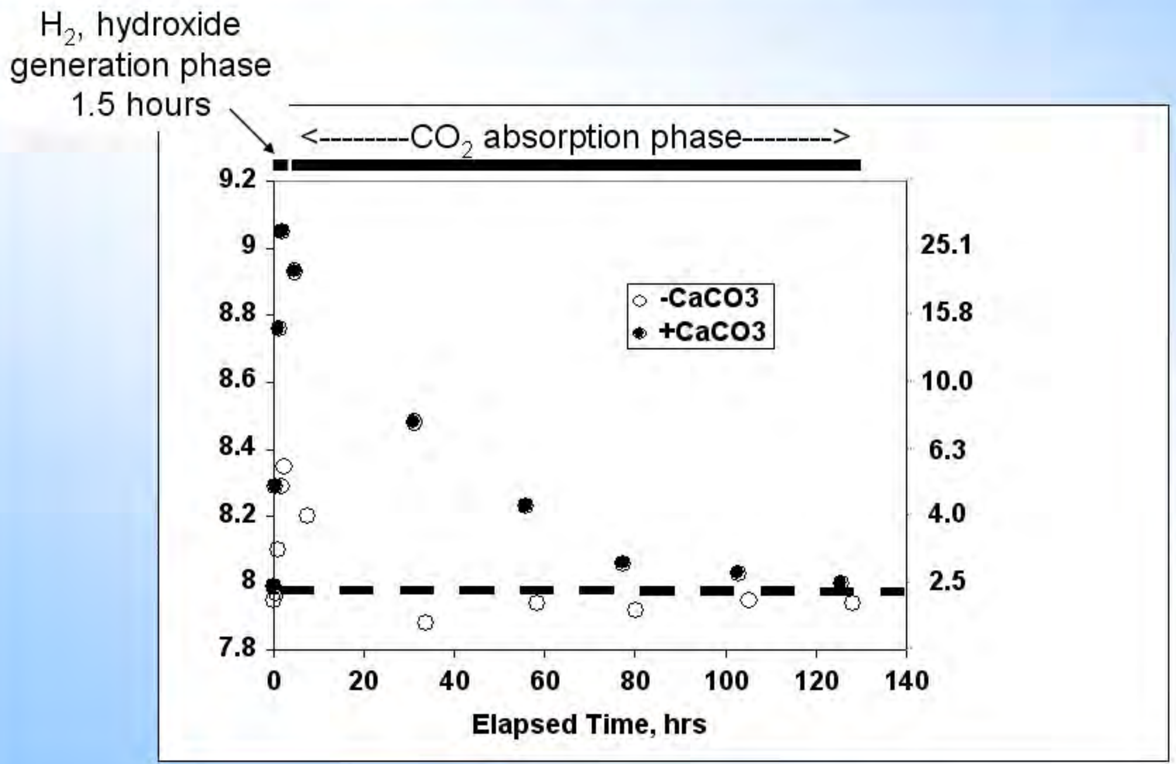
Net gain of $Ca(OH)_2$ leads to net gain of CO_2 at pH 6-9

Experimental Demonstration

Electrode assembly with graphite anode inserted into porous cup containing powdered $CaCO_3$.

Experimental setup with electrode assembly partially immersed in 300 mls seawater. Voltage, amperage, pH, and time readouts on right. pH probe on left.

Experimental Results -
Hydrogen and hydroxide generated, air CO_2 absorbed



ENGEN

Experiment Conclusions:

- Hydroxide increased 5X in the presence of $CaCO_3$
- Excess hydroxide was neutralized after exposure to air via CO_2 absorption and bicarbonate formation. Net CO_2 uptake = 0.6mM = 30% increase in seawater carbon

Implications:

Could globally abundant carbonate minerals (e.g., limestone) and saline water (brines/seawater) be electrolyzed with (stranded) non-fossil electricity to generate hydrogen and solutions that can absorb and sequester CO_2 from air or from point sources?

Important considerations ---->

Consideration #1: Chlorine

- Electrolysis of globally abundant chloride brines (e.g., seawater, groundwater) typically generates chlorine (Cl_2) rather than oxygen (O_2) at the anode; Significant hazard unless consumed or reacted.

- Possible solutions:
  - Adjustment of current density (Bennett, 1980; et al.)
  - Use O_2-selective anodes (Bennett, 1980; et al.)
  - Use non-chloride electrolyte
  - Use ion-selective membranes
  - Combine H_2 and Cl_2 to form acid, HCl; neutralize with silicate minerals (House et al., 2007)

Consideration #2: Energy requirement

In theory:

$CaCO_3 + CO_2 + 2H_20 \rightarrow Ca(HCO_3)_2 + H_2 + 0.5O_2$

ΔG^o = 266kJ/mol = 1680 kWh per tonne CO_2 consumed

Estimated from commercial electrolytic H_2 production:

based on commercial, alkaline electrolytic H_2 production:

360 kJ_e/mole of H_2 produced = 360 kJ_e/mole CO_2 absorbed,

= 2273 kWh_e per tonne CO_2

Potential energy recovery:

If energy recovery via H_2 fuel cell (120 kJ_e/mole H_2 oxidized), then net energy cost =

240 kJ_e/mole CO_2 absorbed or 1515 kWh_e/tonne CO_2

Consideration #3: Reactant and product masses

(kgs/kg H_2 produced)

Atmos. (22) CO_2

Reactants:

(50.6) $CaCO_3$-->

(14.1) Water -->

DC Electricity:

50 kWh_e/kg H_2-->

Saline Electrolysis cell

Products:

--> (37.4) $Ca(OH)_2$ --> (59.4) $Ca(HCO_3)_2$

--> (1) H_2, (9 kg CO_2 avoided)

--> (4.0) O_2/Cl_2

Net CO_2 mitigated: <u>31 kg CO_2 mitigated per kg H_2 generated</u>

Consideration #4: Economics

($/kg H_2 produced)

Atmos. CO_2

Costs:

($0.48) $CaCO_3$ -->

($0.11) Water -->

DC Electricity:

($2.99)@$0.06/kWh$_e$-->

Capital, Operation, And Maintenance:

= ($0.62)

Saline Electrolysis cell

Revenues:

--> $Ca(OH)_2$ ----> ($0.66) $Ca(HCO_3)_2$

--> H_2 ($0.27 revenue from CO_2 avoidance @ $0.03/kg CO_2)

--> ($0.04) O_2

$4.20 (gross cost) - $0.97 (revenue) = <u>$3.23, net cost/kg H_2 produced</u>

commercial H_2 from NG reforming = $1 - $1.50/ kg H_2

Other Potential Revenue, Benefits, Cost Savings

- Use of free $CaCO_3$
  - 20% of commercial limestone production is waste
- The $Ca(HCO_3)_2$ formed may have industrial or environmental value
  - Use as a buffering agent or chemical feed stock
  - Add to ocean to offset effects of ocean acidity
- Local H_2 oxidation in fuel cell
  - Energy storage/recovery from intermittent, renewable energy (wind, solar, tidal, etc)
  - Potable water from brine: $H_2 + 0.5O_2 \text{ ---> } H_2O$

Large-Scale Applications

Site large-scale electrolysis operations at the convergence of abundant water/brine, non-fossil energy, and limestone/ carbonate resources, e.g.:

The Ocean -

- Massive potential electrolyte
- Massive energy, $2x10^6$ TWh/yr
- Massive $CaCO_3$ resources
- Largest CO_2 absorber; >300GT CO_2/yr; 70% of earth's surface

Plenty of Carbonate:

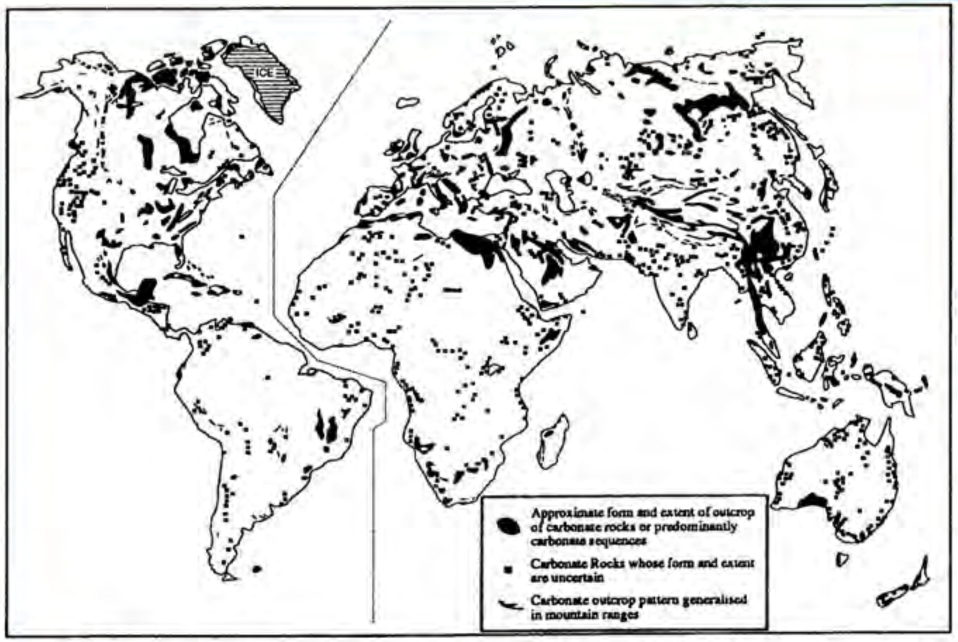
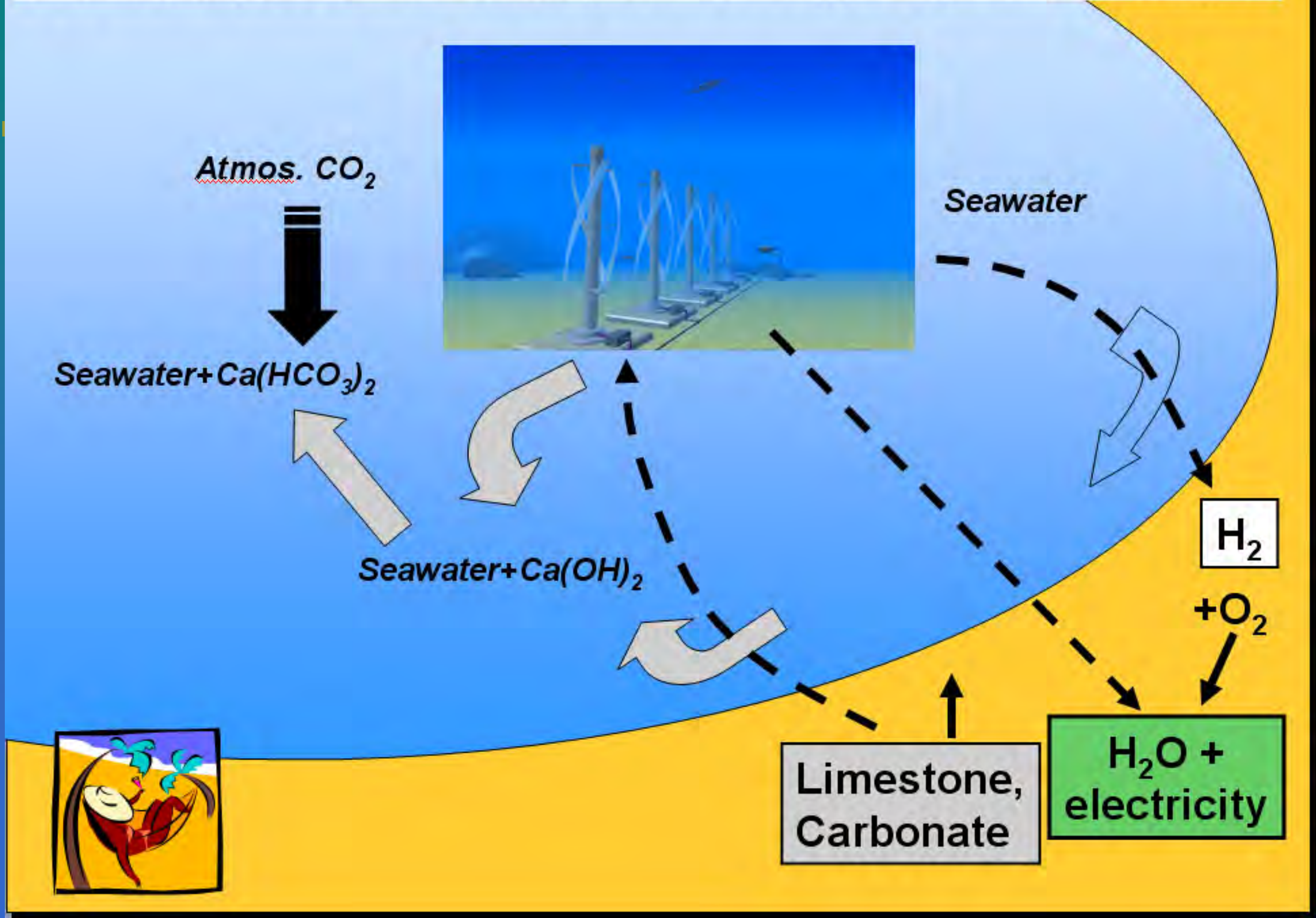


Figure 1.1. Major outcrops of carbonate rocks, most of which exhibit karstification at least to some extent (after Ford & Williams 1989).

For Example: Ocean-based, carbon-negative, tidal hydrogen



Save the Reef (s)

By convert limestone to calcium bicarbonate via a (proprietary) fuel cell which absorbs CO2, produces H2 and O2, reduces ocean salinity and provides reef re-building material, AND

Develop a new cost-effective highly carbon negative process to convert -

Renewable Energy → Hydrogen

The keys to cost effectiveness are –

1. site selection – limestone on a coast with copious marine energy
2. expertly developed fuel-cell system – optimal catalysts & electrodes

Seawater Electrolysis

- **"Bio-Rock"** is the brainchild of scientist Thomas Goreau and the late architect Wolf Hilbertz. The two have set up similar structures in some 20 countries. When hooked up to a low-voltage energy source limestone—a building block of reefs—naturally gathers on the metal.

Electricity Revives Bali Coral Reefs

Associated Press Dec 4, 2007

Now they are coming back, thanks to an unlikely remedy: electricity.
The coral is thriving on dozens of metal structures submerged in the bay and fed by cables that send low-voltage electricity, which conservationists say is reviving it and spurring the growth.
As thousands of delegates, experts, and activists debate climate at a conference that opened this week on Bali, the coral restoration project illustrates the creative ways scientists are trying to fight the ill-effects of global warming

Global map of Coral Reefs

- Coral reefs have the richest marine ecologies
- 300M people to our north live on islands and depend on coral reef fisheries